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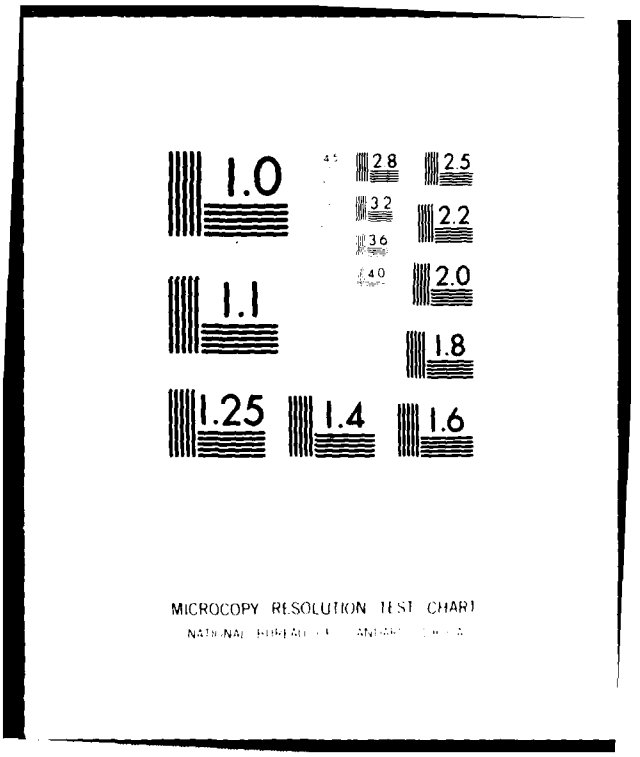
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TECHNICAL REPORT NO. 110

READY CAGE EXCHANGE REACTIONS OF ICOSAHEDRAL HYDRIDOPHOSPHINORHODACARBABORANES.

By

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SUMMARY

Four coordination sites of formally six coordinate Rh^{III} carbaborane complexes have been replaced in facile, single-step thermal reactions.

Ready Cage Exchange Reactions of Icosahedral Hydridophosphinorhodacarbaboranes.

by Todd B. Marder, Judith A. Long and M. Frederick Hawthorne*
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Summary: Four coordination sites of formally six coordinate Rh^{III} carbaborane complexes have been replaced in facile, single-step thermal reactions.

Several reports have appeared concerning thermal ligand exchange reactions of ferrocene and related complexes[1-4], arene chromium tricarbonyl complexes[5], and photolytic exchanges using $[(\eta^5\text{-}C_5H_5^{\eta})_2MCl_n^{\eta}]$(M=V,Ti,Zr,Hf;n=0,1,2)[6,7]. Most of the thermal reactions seem to require vigorous conditions and the yields are in general rather low. However, Khan and Dormond have recently reported facile, thermal exchange of cyclopentadienyl rings in certain Ti complexes[8,9]. In the course of our studies on homogeneous alkene hydrogenation catalyzed by phosphinometallocarbaboranes[10-13] we have discovered a general and facile method for transferring the $(PPh_3^{\eta})_2^{\eta}Rh$ fragment from one carbaborane cage to another.

Figures 1 & 2

Complex IVd(see fig. 1) can be prepared by the reaction of the Me_4N^+ salt of Id (see fig. 2) with $[(PPh_3)_3RhCl]$ in MeOH at room temperature [14]. † The product gradually precipitates as a dark orange powder. Complex IVa can be obtained directly as a yellow-orange powder by the analogous reaction with anion Ia as well as by the reaction of Ia with previously prepared IVd in refluxing ethanol. These reactions are very clean and the rhodium complexes are isolated in excellent yield. Indeed, in the latter reaction anion Id is recovered in

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† Compound IVe was characterized by X-ray crystallography. Satisfactory analytical data were obtained for all other new compounds.

good yield. To ensure recovery of pure metal complexes, approximately 10% excess anion was used, whereas in order to isolate pure anion, a 10% deficiency of reactant anion was used. The metal complexes were isolated directly, by filtration. The anions were recovered from the filtrate by removal of the solvent *in vacuo*, followed by a benzene wash to remove any remaining rhodium complex. Purity of the rhodium complexes was determined by ^{1}H or $^{31}P\{^{1}H\}$ NMR spectroscopy.

We have established the following order for ease of displacement of the carbaborane anion (see fig. 1): Ie>Ic>Id>Ia>II~III. Under the conditions employed most of the exchanges are complete in a few hours. However, in the reaction of IVa with III, ca. 10% of IVa was present even after 3 1/2 days and in the reaction of IVa with II, trace quantities of IVa were present after 2 days. When complex V was reacted with 10 equivalents of Ia for 6 days, the resulting ratio of V/IVa was ca. 7/1. *There was no exchange observed in the reactions of either V with III or VI with II.* Addition of up to 10 equivalents of PPh_3 appeared to have no effect on either the rate or product composition.

The reaction of the carbon-deuterated analog of IVa, namely IVb, with 2 equivalents of isotopically normal anion Ia showed a significant amount of carbaborane C-H incorporated into the isolated rhodium complex after about one week. A sample of IVb refluxed in ethanol for one week showed no carbaborane C-H in the proton NMR spectrum. When IVc was reacted with anion Ia, which had been specifically deuterated at the B-H-B bridging site[15], the IVa recovered showed Rh-D and no Rh-H.‡ The source of the Rh-H is therefore the acidic B-H-B bridge of the incoming carbaborane anion (as has been shown for the preparation of IVa from $[(PPh_3)_3RhCl]$[16]).

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‡Determined by ^{1}H NMR (δ_{Rh-H} = -8.40, CD_2Cl_2) and IR (ν_{Rh-H} = 2080,2120cm^{-1}; ν_{Rh-D} =1520cm^{-1}).

If we assign three coordination sites and a formal -2 charge to the carbaborane cage, one site and a -1 charge to the hydride ligand and one site each to the two PPh_3 groups, then the cage exchange reaction formally replaces four coordination sites of a six-coordinate Rh^{III} complex in a single clean reaction. Further mechanistic studies are in progress and will be reported at a later date.

We thank Dr. R.A. Grey for preliminary results, the University of California for a Regents' Fellowship (T.B.M.) and a Chancellor's Fellowship (J.A.L.) and Matthey Bishop Inc. for a generous loan of rhodium trichloride.

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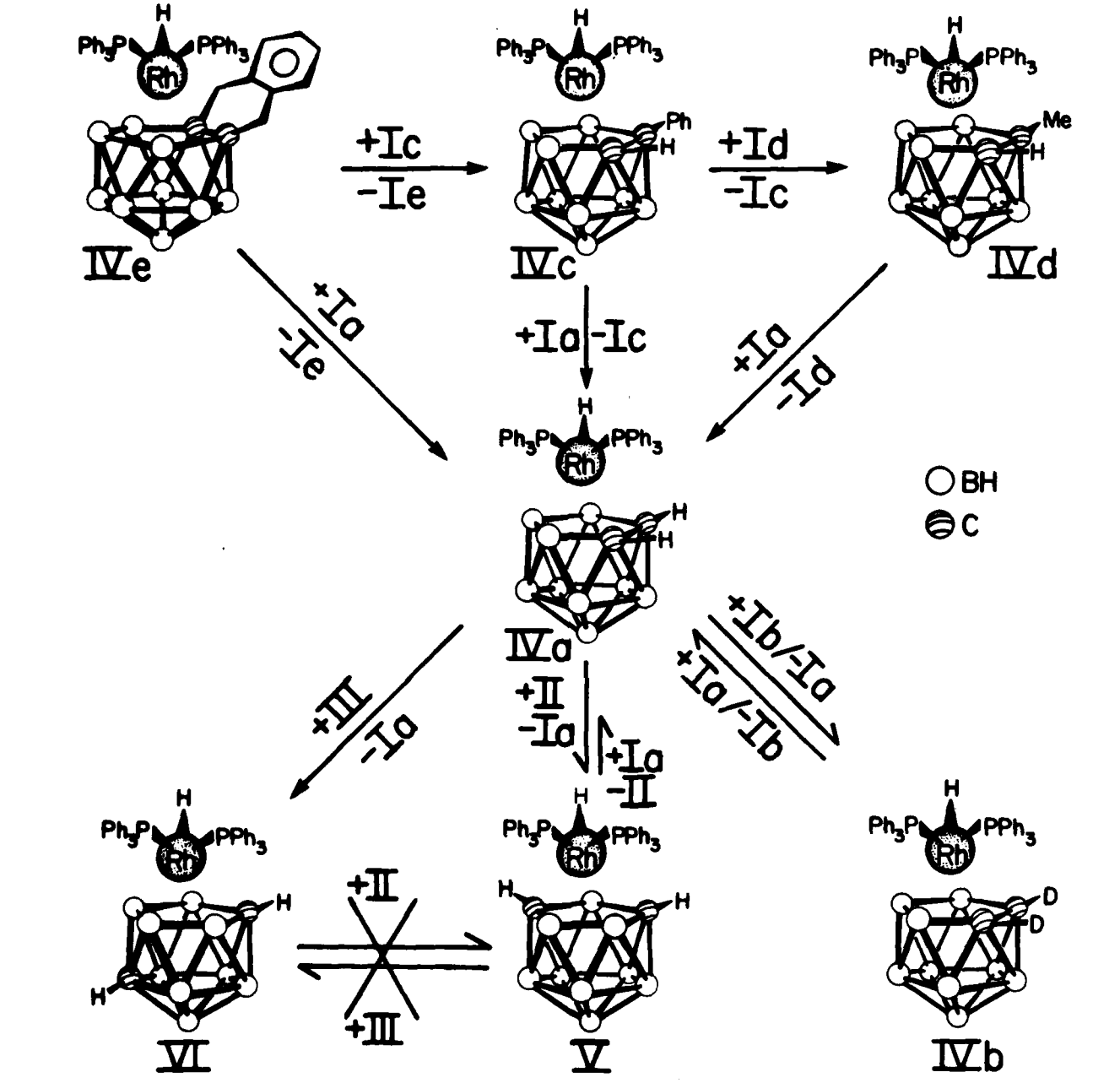
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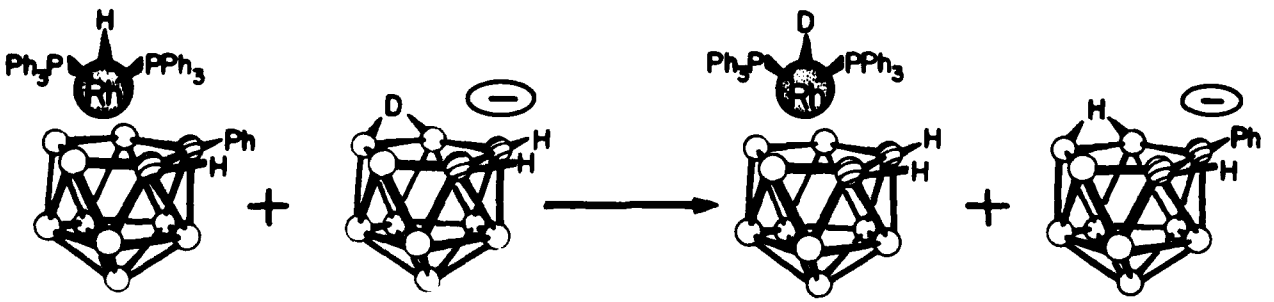

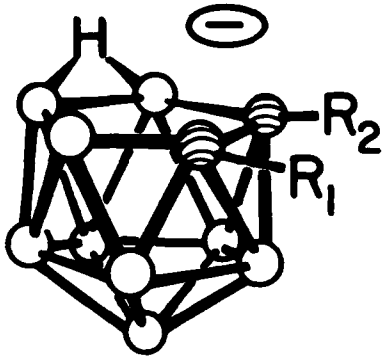

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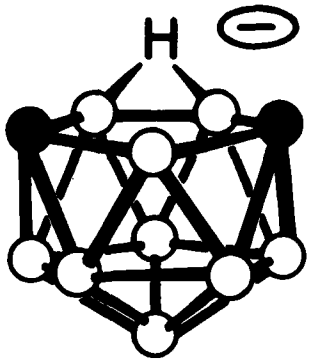

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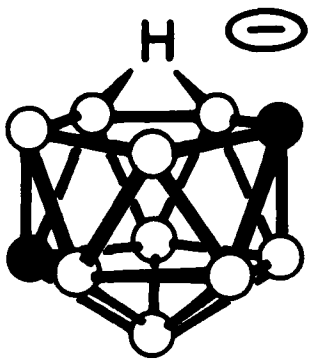


III

○ BH

● CH

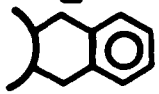
◎ C

a; $R_1 = R_2 = H$

b; $R_1 = R_2 = D$

c; $R_1 = H$, $R_2 = Ph$

d; $R_1 = H$, $R_2 = Me$

e; $R_1R_2 =$ 

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Four coordination sites of formally six coordinate Rh^{III} carbaborane complexes have been replaced in facile, single-step thermal reactions.

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